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Plenary Session

Kentucky Water Resources Research Institute, University of Kentucky

NANOCOMPOSITE MEMBRANES FOR WATER PURIFICATION

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Water pollution is a serious concern in all aspects of society. Pollutants have two main origins: organic compounds and heavy metals. These contaminants have high interest because of their persistence in nature and difficulties related with their treatment and/or elimination. In this field, membrane-based separation processes have been widely used in water detoxification, water purification and waste water treatment.

Stimuli-responsive polymers have been used extensively due to their unique and excellent physical and chemical responses to changes in physiological conditions and they have been applied in different areas: such as, drug delivery, bioseparation or tissue engineering. Combining these polymers with different membranes results in responsive membranes for regulated permeation of pH, temperature or light, etc. Development of nano-structured material synthesis using responsive membranes that contain ion exchange groups is a promising research field with potential applications in water pollution, energy, catalysis and mining.

In our work, different Hydrophylized Polyvinylidene Fluoride (PVDF) membranes (flat sheet, spongy sheet and hollow fiber) were used as support due to their chemical resistance properties and good thermal stability. Immobilized metallic nanoparticles in the PVDF-responsive polymer membrane were used for water detoxification of chloro-organics (Trichloroethylene and Polychlorinated biphenyls) and metal capture (Selenium and Arsenic). In addition, we also extended our work in the characterization of the nanostructured material and its responsive behavior on solute permeability.

This research is supported by the NIEHS-SRP grant P42ES007380 and by NSF EPSCoR grant. Hollow fiber Membranes were synthesized at the Singapore Membrane Technology Center, NTU (Singapore, Singapore). Flat sheet and spongy membranes used are from EMD Millipore (Billerica MA, USA), Ultura (Oceanside CA, USA) and synthesized in our lab.

NOTES

NANOFILTRATION MEMBRANES FOR WATER REUSE AND TOXIC INORGANICS REMOVAL FROM COAL-FIRED POWER PLANT WATER

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Nanofiltration (NF) membranes have been shown to be highly effective for the selective separation of ions from processed water in a variety of industries. The concentrations of dissolved solids and toxic metal ions are particularly a concern in the operation of wet flue gas desulfurization systems in coal-fired power plants. NF membranes can be used to remove high dissolved solids concentrations from scrubber water, achieving high water recovery for reuse in the process. Actual scrubber water, provided from Georgia Power's Plant Bowen (~10,000 ppm TDS, ~1 ppm Se) was recovered using spiral wound membrane module (0.59 m^2 membrane area) configurations of NF membranes developed in collaboration with Sepro Membranes. The selective rejection of divalent over monovalent ions in the NF membranes was advantageous for recovering the scrubber water which consisted of primarily of Ca^{2+} and Mg^{2+} with counter-ions consisting of Cl^- and SO_4^{2-}. The membranes were shown to highly reject selenium (97.3%) and other toxic inorganics present (90.9% As; 96% Ni). Water recovery exceeding 80% was achieved while maintaining over 60% rejection of dissolved solids. At higher water recovery, calcium sulfate precipitation was observed in the process, and aspects related to gypsum precipitation were studied. The use of actual scrubber water being recovered with large scale membrane modules best reflects real-life process conditions. The results prove that high water recovery and the rejection of toxic inorganics can be achieved for Coal-Fired Power Plant water.

ACKNOWLEDGEMENTS:

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THERMAL ANALYSIS AND RAMAN STUDIES OF THE PHOTOCATALYTIC DEGRADATION OF ORGANIC POLLUTANTS

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The presence of organic compounds such as pharmaceuticals, road and construction runoff, and farm waste has been detected in drinking water with increasing frequency, and at increasing concentrations. Photocatalytic degradation is an emerging technology which has gained traction in the removal of such harmful organic compounds in water. Although much is understood about the overall rates of conversion of toxic compounds, the chemical mechanisms underlying their degradation are not adequately understood. We have studied the chemical and physical processes involved in photocatalytic degradation processes using a variety of different approaches, and on many different classes of compounds, in an effort to discern general trends to help explain the mechanisms underlying this important technology.

We use Raman spectroscopy to provide faster kinetics to unravel the details of photocatalytic reactions with the instrument shown in Figure 1. Here, a flowing reactor allows us to monitor the Raman spectra of many different compounds simultaneously,

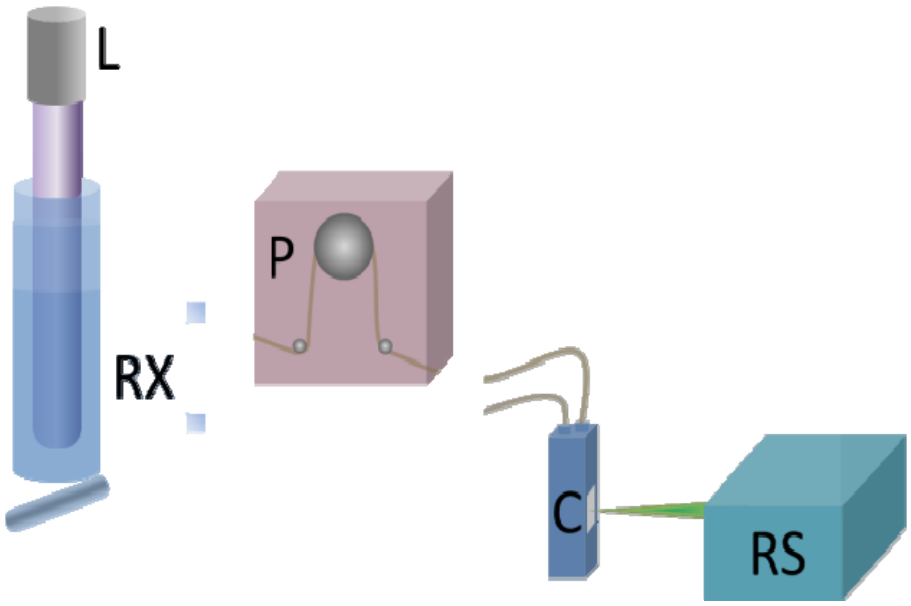

Figure 1. Experimental setup, showing UV lamp source (L) emitting into the center of the reactor (RX), with reaction mixtures pumped (P) to a cuvette (C) in a darkened enclosure for Raman analysis by an appropriate spectrometer (RS).

which has already led to the identification of the most important reactive pathways for the degradation of the x-ray contrast agents diatrizoate and iohexol. Recent improvements to our process include the introduction of surface-enhanced Raman spectroscopy (SERS) and the development of a pulsed-laser Raman spectrometer capable of collecting twenty spectra per second. Our SERS experiments allow us to identify compounds at the micromolar concentration level by adhering analytes to gold nanoparticles in solution. Quantitative results can be accomplished with a co-adhered internal standard. These advances will lead to mechanistic details necessary to guide the development of future technologies that will optimize the use of photocatalytic degradation for municipal districts or for widespread pollution remediation efforts.

In parallel with our Raman experiments, we have performed thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) experiments which investigate the binding of various analytes (polycyclic aromatic hydrocarbons, pesticides, x-ray contrast media, and antibacterial agents) to the photocatalyst TiO_2. Mass loss of some analytes is detected at different temperatures for the pure compound than when in the presence of TiO_2, indicating that certain analytes bind more strongly to the photocatalyst than others. Since binding is a pre-requisite for direct oxidation by electron holes, we are able to conclude that compounds which are not functionalized with heteroatom groups (i.e., do not contain atoms other than carbon and hydrogen) are unlikely to undergo direct oxidation by holes. Trends also appear in the DSC results that indicate that the binding in some cases may be due to rearrangement of the photocatalyst structure. Although this does not occur to a substantial enough extent that it can be detected with crystallographic analysis, it does suggest that the nature of the analyte-photocatalyst interaction warrants further study. Faster (real-time) Raman experiments coupled with quantum computational chemistry and molecular dynamics simulations will continue to enhance our understanding of the molecular processes that undergo this important new technology. These studies may prove particularly important in the development of next generation photocatalysts as such approaches come into more widespread usage.